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MASS SPECTRAL FRAGMENTATION OF A NOVEL CYCLOOCTANE: 2,4-DIMETHYL-7,7-DINITRO-1,3,5-TRIOXACYCLOOCTANE

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PROJECT 2303

AIR FORCE SYSTEMS COMMAND
UNITED STATES AIR FORCE

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A novel cyclooctane containing structural features unique to both geminal polynitroalkanes and cyclic trioxane acetals afforded an initial electron impact fragmentation analogous to cyclic acetals. Only in the latter stages of the fragmentation pathway did specied appear that are characteristic of geminal polynitroaliphatic and nitroalkane molecules.

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By

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Capt Scott A. Shackelford

TECHNICAL REPORT FJSRL-TR-80-0012

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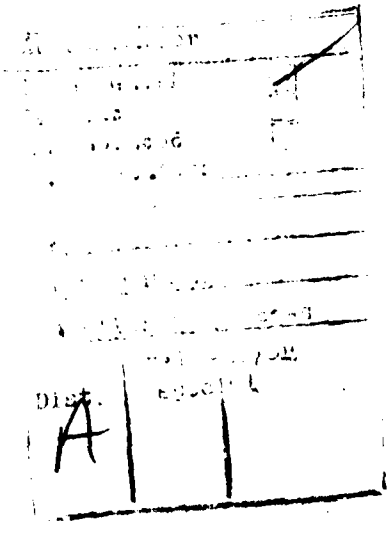

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PREFACE

This document, FJSRL-TR-80-0012, summarizes detailed mass spectroscopic studies done on the novel cyclooctane: 2,4-dimethyl-7,7-dinitro-1,3,5-trioxacyclooctane. The work described here was done under Work Unit 2303-F3-01 and was not previously published by the authors.

TABLE OF CONTENTS

LIST OF SCHEMES

LIST OF TABLES

INTRODUCTION

A novel cyclooctane containing structural features unique to both geminal polynitroalkanes and cyclic trioxane acetals afforded an initial electron impact fragmentation analogous to cyclic acetals. Only in the latter stages of the fragmentation pathway did species appear that are characteristic of geminal polynitroaliphatic and nitroalkane molecules.

The subject compound, 2,4-dimethyl-7,7-dinitro-1,3,5-trioxacyclooctane (I), contains two distinctly different chemical structural features representative of a substituted cyclic trioxane acetal and a geminal polynitroalkane. While separate electron impact studies have been reported for cyclic acetals (e.g., dioxanes and trioxanes)[2,3] and for nitrated alkane derivatives[4-6], the limited nitroalkane mass spectral studies offer no clue to the geminal polynitroalkane structure's electron impact stability. Compound I allows a direct intramolecular comparison of electron impact fragmentation stabilities between a cyclic trioxane acetal structure and the geminal dinitroalkane grouping because of its unique incorporation of both structural features in a single compound.

RESULTS AND DISCUSSION

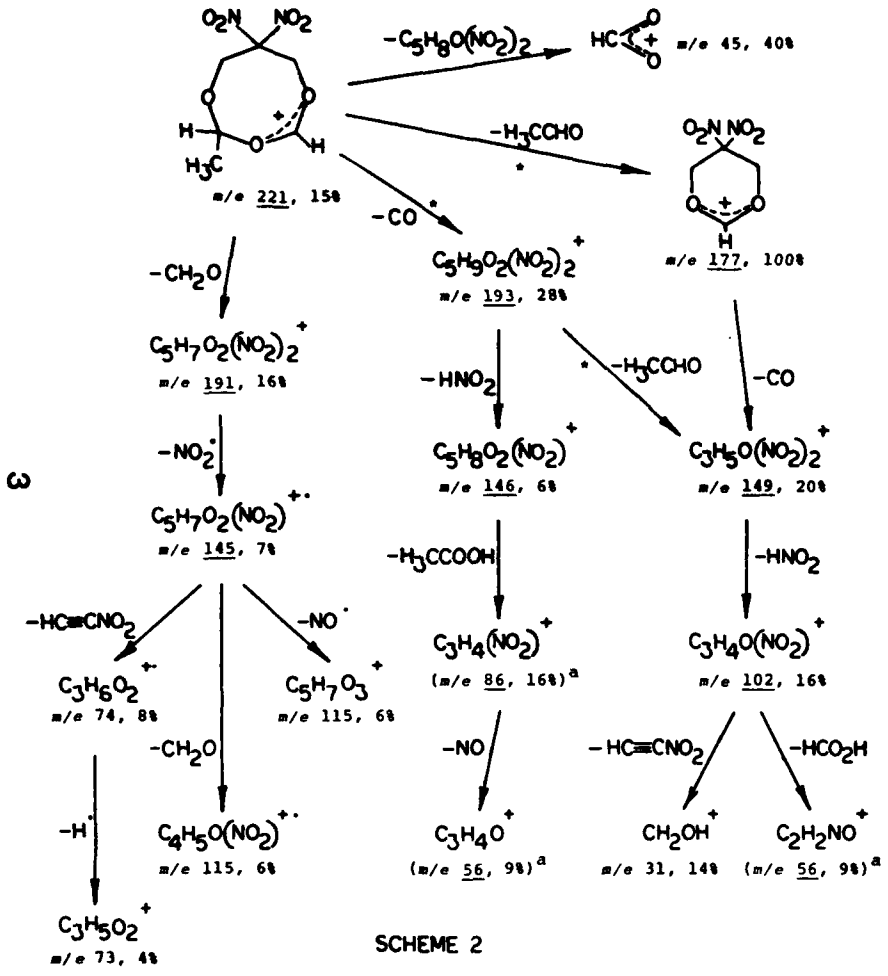
Neither nitro- nor polynitroalkanes form an appreciable molecular ion[4-6]. Polynitroalkanes characteristically lose NO_2 and NO; while nitroalkanes generally release NO_2 and HNO_2 to yield charged alkyl species that undergo further fragmentation. The geminal polynitroalkane, 2,2-dinitropropane, a compound closely resembling the polynitroalkane structure in (I), gives predominantly NO^+ (m/e 30)[6]. A moderately intense ion at m/e 39 $(C_3H_3)^+$ is generated by stepwise loss of NO_2, then NO with oxygen migration to the α carbon to form a charged acetone species, and finally, loss of an OH radical.

An appreciable ion at m/e 43 $(CH_3CO)^+$ was also observed and postulated to form from the charged acetone species by loss of a methyl radical[6].

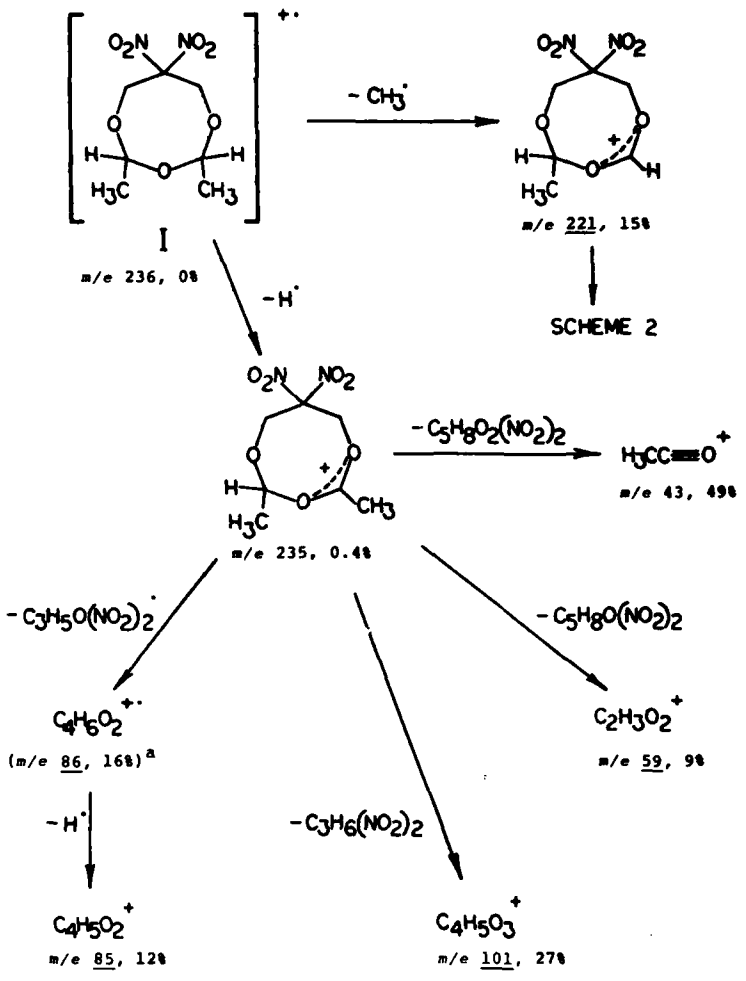
Cyclic ethylene acetals likewise do not afford a molecular ion, but lose an alkyl radical to form resonance stabilized oxonium ions[2]. Symmetrical trioxane closely resembles the acetal chemical structure found in (I) and exhibits the loss of one methylene hydrogen atom to form an oxonium ion[3]. Subsequent fragmentation appears to be dictated by the resultant oxonium ion structure.

The initial fragmentation by (I) follows the same electron impact cleavages observed for in normal alicyclic acetals (Scheme 1)[2,3]. The spectrum shows no molecular ion at m/e 236 (Table I), and loss of a methyl radical to produce the m/e 221 oxonium ion is heavily favored over a hydrogen atom cleavage to yield the m/e 235 oxonium species[2,3]. The lesser m/e 235 oxonium fragment appears to form four additional ions at m/e 101, 86, 59, and 43, all by loss of neutral species containing the intact geminal dinitro group. The m/e 86 ion $(C_4H_6O_2)$ is one of two mass doublets found and confirmed by high resolution mass spectral analysis.

Fragmentation reactions generated from the more favored m/e 221 oxonium ion produce four additonal ions (Scheme 2); however, only one species (m/e 45), characteristic of cyclic acetal fragmentation noted of the m/e 235 ion, is formed by the loss of a neutral geminal dinitroalkane molecule. The three remaining ions produced from the eight-membered m/e 221 cyclic oxonium ion are likely six-membered cyclic geminal dinitroalkyl oxonium derivatives formed from normal cyclic acetal fragmentation mechanisms. The m/e 193 molecule forms by a CO loss[2]; the m/e 191 oxonium species is generated by the loss of formaldehyde (CH_2O); and the base peak, m/e 177,



SCHEME 2



SCHEME 1

(*) metastable, (a) mass doublet, Underlined masses determined by high resolution analysis.

TABLE 1. RELATIVE ION ABUNDANCES

m/e	Percent	Formula
236 $[M]^{+\cdot}$	0	$C_7H_{12}N_2O_7$
235	0.4	$C_7H_{11}N_2O_7$
221	15	$C_6H_9N_2O_6$
193	28	$C_5H_9N_2O_6$
191	16	$C_5H_7N_2O_6$
177	100	$C_4H_5N_2O_6$
149	20	$C_3H_5N_2O_5$
146	6	$C_5H_8NO_4$
145	7	$C_5H_7NO_4$
115	6	$C_4H_5NO_3$ or $C_5H_7O_3$
102	16	$C_3H_4NO_3$
101	27	$C_4H_5O_3$
86 (doublet)	16	$C_3H_4NO_2$ $C_4H_6O_2$
85	12	$C_4H_5O_2$
74	8	$C_3H_6O_2$
73	4	$C_3H_5O_2$
59	9	$C_2H_3O_2$
56 (doublet)	9	C_2H_2NO C_3H_4O
45	40	CNO_2
43	49	C_2H_3O
31	14	CH_2OH
30	33	CH_2O, NO(?)

Underlined ions confirmed by high resolution mass spectrometry.

forms from the m/e 221 oxonium ion splitting out an acetaldehyde molecule (CH_3CHO). Meta stable peaks at m/e 168.5 and m/e 141.5 establish the 193 and 177 ions respectively as having the common m/e 221 precursor.

Only at this point do fragmentation mechanisms characteristic of nitroalkane or geminal dinitroalkanes begin to appear. While the m/e 193 oxonium ion splits out acetaldehyde in a characteristic cyclic acetal fragmentation to form m/e 149, it also can lose an HNO_2 molecule to yield m/e 146[5]. The m/e 146 fragment continues by splitting out acetic acid to give the second m/e 86 mass doublet ($C_3H_4NO_2$). Loss of NO than affords m/e 56 (C_3H_4O) which also is one ion comprising another mass doublet found in this mass spectrum. The m/e 149 species is associated by a metastable appearing at 115 to the m/e 193 precursor ion. The m/e 149 species also splits out a neutral HNO_2 molecule to yield m/e 102. This molecule can lose formaldehyde to generate the other m/e 56 $(C_2H_2NO)^+$ mass doublet, or it can cleave out mononitroacetylene to eventually provide m/e 30 ($CH_2O^{+\cdot}$) via m/e 31 ($CH_2\overset{+}{O}H$). The m/e 30 fragment could also be attributed to initial formation of NO^+ from the original geminal dinitro alicyclic eight and/or six-membered oxonium molecules since 2,2-dinitropropane affords an intense m/e 30 (NO^+) peak. However, it should be noted that no other transformations characteristic of 2,2-dinitropropane are observed in Schemes 1 and 2. The remaining peak at m/e 191 formed by loss of formaldehyde from m/e 221 initiates the only remaining fragmentation pathway that contains typical nitroalkane or geminal polynitroalkane cleavages. Although a seemingly minor process, m/e 191 cleaves an NO_2 radical to form m/e 145. The m/e 145, fragment like m/e 102, can liberate mononitroacetylene to yield m/e 73 via m/e 74; or, it can form two possible m/e 115 species by losing neutral CH_2O or by undergoing

another characteristic nitroalkane process and cleaving an NO radical. While the m/e 191 fragment could have formed from m/e 235 by loss of acetaldehyde to provide a species analogous to m/e 177, this pathway is ruled out since all reasonable subsequent reactions would lead to charged species not observed in this spectrum.

In summary, the subject compound, 2,4-dimethyl-7,7-dinitro-1,3,5-trioxacyclooctane (I), represents a molecule of novel chemical structure that contains features common to both alicyclic trioxane acetals and geminal dinitroalkanes. A mass spectrum typical of alicyclic acetals predominates and produces cyclic oxonium ions and low molecular weight CHO molecules as major species. Only relatively late in the fragmentation mechanism are transformations observed that represent pathways characteristic of nitro- and polynitroalkanes. There seems to be a reversal in the fragmentation pattern of the nitroalkane species in that the geminal dinitroalkane ions resulting from (I) parallel mass spectral fragmentations observed for pure mononitroalkanes[4,5], while mononitroalkane ions from (I) generally fragment as did polynitroalkanes in a previous study[6]. The results described herein suggest the geminal dinitroalkane group is more stable to electron impact fragmentation than one might suspect (a priori). Its electron impact stability apparently exceeds that exhibited by the cyclic acetal structure as demonstrated by the subject compound whose novel chemical architecture provides a direct intramolecular comparison between these two structural groupings.

EXPERIMENTAL

The mass spectra cited were obtained with a DuPont Instrument 21-491 double focusing mass spectrometer at an ionizing voltage of 78 eV and source temperature around 180°C. The sample was introduced into the mass spectrometer by a direct insertion probe. The compound, 2,4-dimethyl-7,7-dinitro-1,3,5-trioxacyclooctane (mp 54-57°C), gave the following analysis: (Found: C, 35.4; H, 4.9; N, 12.0. $C_7H_{12}N_2O_7$ required C, 35.6; H, 5.1; N, 11.9).

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REFERENCES

1. Present Address: L-402, Lawrence Livermore Laboratory, Livermore, CA 94513.

2. J. T. B. Marshall and D. H. Williams, Tetrahedron 23, 321 (1967).

3. H. B. Budikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, San Francisco, pp. 257-258 (1967).

4. J. Collin, Bull. Soc. Roy. Sci. Liege 194 (1954).

5. R. T. Aplin, M. Fischer, D. Becher, H. Budzikiewicz, and C. Djerassi, J. Am. Chem. Soc. 87, 4888 (1965).

6. J. T. Larkins, F. E. Saalfield, and L. Kaplan, Org. Mass Spectrum. 2, 213 (1969).